

303627

EVOLUTION OF CHEMICALLY PROCESSED AIR PARCELS IN THE LOWER STRATOSPHERE

Richard S. Stolarski, Anne R. Douglass, and Mark R. Schoeberl

Laboratory for Atmospheres
NASA Goddard Space Flight Center
Greenbelt, Maryland 20771, USA

ABSTRACT

Aircraft, ground-based, and satellite measurements indicate large concentrations of ClO in the lower stratosphere in and near the polar vortex (Anderson, et al., 1989; Brune et al., 1990; de Zafra, et al., 1987; Waters et al., 1993). The amount of local ozone depletion caused by these large ClO concentrations will depend on the relative rates of ozone loss and ClO recovery. ClO recovery occurs when NO_x, from HNO₃ photolysis, reacts with ClO to form ClONO₂. We show that air parcels with large amounts of ClO will experience a subsequent ozone depletion that depends on the solar zenith angle. When the solar zenith angle is large in the middle of winter, the recovery of the ClO concentration in the parcel is slow relative to ozone depletion. In the spring, when the solar zenith angle is smaller, the ClO recovery is much faster. After ClO recovery, the chlorine chemistry has not returned to normal. The ClO has been converted to ClONO₂. ClO production from further encounters with PSCs will be limited by the heterogeneous reaction of ClONO₂ with water. Large ozone depletions, of the type seen in the Antarctic, occur only if there is significant irreversible denitrification in the air parcel.

INTRODUCTION

We have developed a version of our photochemistry model (Douglass et al., 1989) to calculate chemical changes occurring along the path of a stratospheric air parcel. In this study we apply the model to the simple case of a parcel which is fixed at a given latitude and altitude; 50°N and 20 km. The chemistry of the parcel is initialized by assuming that the air has been fully processed by heterogeneous reactions on the surface of NAT particles; i.e. all of the reactive nitrogen is HNO₃ and all of the inorganic chlorine is ClO or Cl₂O₂ (Jones et al., 1990; Brune et al., 1990; Fahey et al., 1990). Parcels are started at the beginning of each month of the northern winter and spring (November through April) and are allowed to evolve chemically for 30 days. At this point, ozone loss greater than that expected from normal photochemistry has ceased. Details of the assumed initial conditions are shown in Table 1.

Starting Date	January 1 or April 1
Pressure	50 mbar
Temperature	210 K
ClO + 2Cl ₂ O ₂	2.5 ppbv
ClONO ₂	0.0
HCl	0.0
HNO ₃	15 ppbv
NO _x	0.0

Table 1. Parcel initialization conditions. Integration of the gas-phase chemical equations is carried out for 30 days from starting date.

MODEL RESULTS

Ozone loss calculated from two model runs are shown in Figure 1. One run begins January 1 while the other begins April 1. On the first day after initialization,

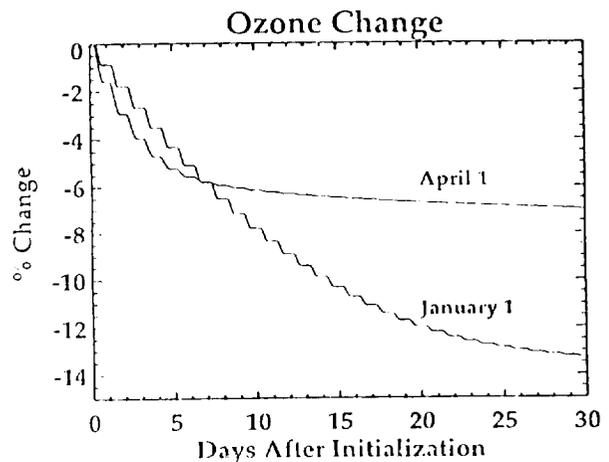


Fig. 1. Calculated ozone change as a function of time after parcel initialization. Results are shown for two parcels, one initialized on January 1, the other on April 1.

both parcels have about the same ClO concentration and lose ozone at the same rate. The parcel released on April 1 experiences a longer period of sunlight and thus loses more ozone. As the parcels evolve, the one released on April 1 exhibits a rapid recovery of ClO as illustrated in Figure 2. Thus, the rate of ozone loss for the April 1 parcel diminishes each day such that by day 4, the total ozone lost is the same as that lost by the January 1 parcel despite the difference in the length of day. By day 6, the cumulative ozone loss in each of the parcels is the same and on all succeeding days, the ozone loss is greater for the parcel released on January 1. The somewhat surprising result is that the parcel which was fully processed by January 1 lost 13% of its initial ozone, while the parcel which was fully processed on April 1 lost only 7% of its initial ozone.

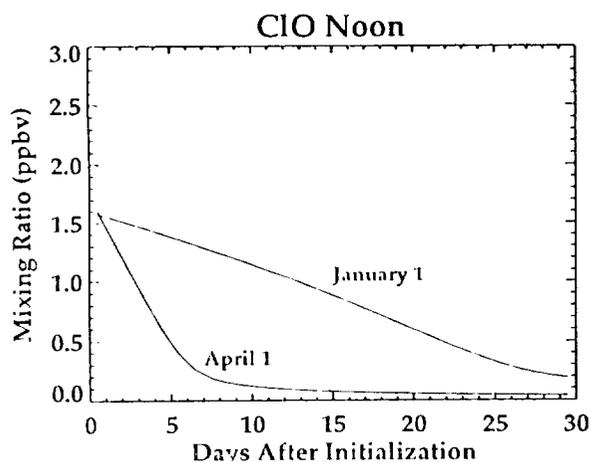


Fig. 2. Calculated noon ClO mixing ratio as a function of time after parcel initialization. Actual calculated ClO exhibits a strong diurnal variation with a noon maximum.

The recovery of the ClO concentration is controlled by NO_x which is generated by the photolysis of HNO_3 . Because the parcel has a very high ClO concentration, the NO_x generated is rapidly converted to ClONO_2 . For the April 1 parcel, the ClONO_2 concentration rises rapidly to 2.5 ppbv, using up all of the available chlorine as illustrated in Figure 3. The January 1 parcel shows a slower rise, but still goes to 2.5 ppbv after 30 days. Figure 4 illustrates that the chlorine nitrate concentration rises at almost exactly the rate of the disappearance of HNO_3 . When the ClONO_2 concentration reaches 2.5 ppbv, no more ClO is available, and NO_x begins to accumulate. At the end of 30 days, the HCl concentration is barely more than 0.2 ppbv for the April 1 parcel and about 0.1 ppbv for the January 1 parcel.

The reason for the change in the relative efficiency of ozone loss to ClO recovery can be understood by examining the photolysis rates for Cl_2O_2 and HNO_3 . Figure

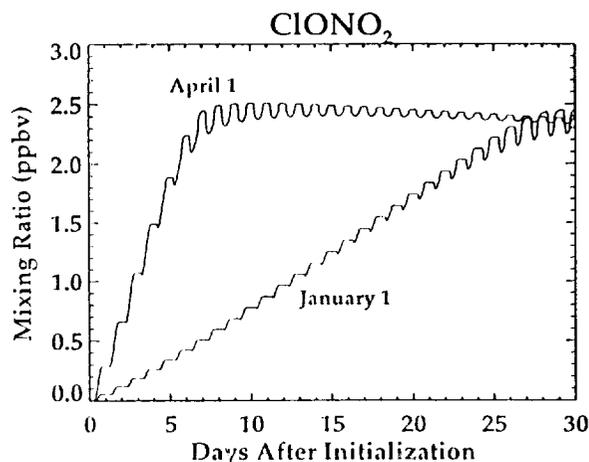


Fig. 3. Calculated ClONO_2 mixing ratio as a function of time after parcel initialization.

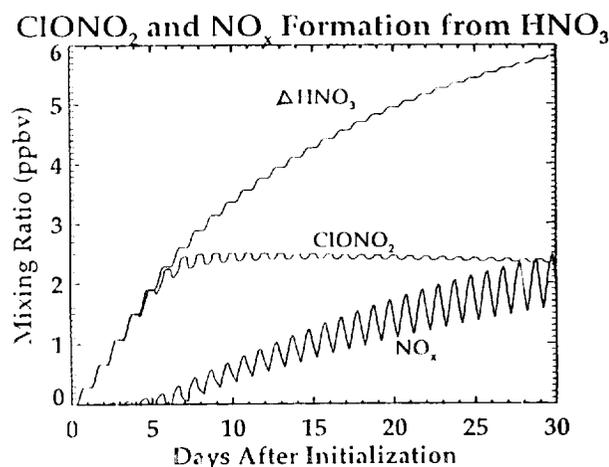


Fig. 4. Comparison of calculated ClONO_2 mixing ratio as a function of time with the rate of disappearance of HNO_3 . When all of the chlorine is used up to form ClONO_2 , the NO_x mixing ratio begins to rise.

5a shows the diurnal variation of the HNO_3 photolysis rate on January 1 compared to April 1. Figure 5b shows the same thing for the photolysis rate of Cl_2O_2 . Cl_2O_2 , because of its near uv absorption, is photolyzed about 70% as rapidly on January 1 as on April 1. HNO_3 , on the other hand, is photolyzed only about 35% as rapidly on January 1. For a given amount of ClO, the rate of ozone destruction by the ClO dimer cycle is determined by the Cl_2O_2 photolysis rate. It can be seen from Figure 5 that the sun effectively rises faster for ozone destruction than it does for ClO recovery.

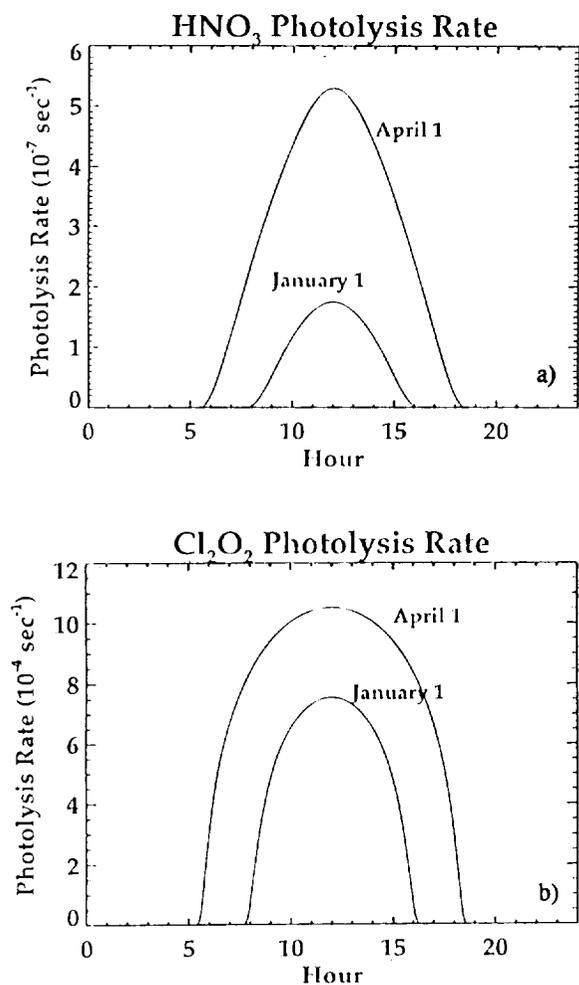


Fig. 5. a) Diurnal cycle of the HNO₃ photolysis rate for January 1 and April 1, b) same for Cl₂O₂.

CONCLUSION

Ozone depletion occurring in parcels of lower stratospheric air, which have been processed through a PSC, is limited by the recovery of the high ClO concentrations to chlorine nitrate. Parcels processed in the middle of winter showed more subsequent ozone depletion than those processed in the spring. A parcel which was initialized on January 1 with all of the chlorine as ClO and Cl₂O₂, and all of the reactive nitrogen as HNO₃, lost 13% of its ozone in the next 30 days. A parcel similarly initialized on April 1, lost only 7% of its ozone in 30 days. The explanation has been shown to be related to the relative photolysis rates of Cl₂O₂ and HNO₃, which govern the competition between ozone loss and ClO recovery.

If the chemically perturbed air from these parcels is processed through a subsequent PSC, recovery of ClONO₂ to ClO cannot occur via reaction with HCl because of the slow recovery of HCl. The effect of further PSC processing will be limited by the reaction of ClONO₂ with water. However, if the air has been denitrified, large ozone depletions can occur because chlorine nitrate formation will be inhibited. In this case, recovery will be controlled by the resupply of active nitrogen to the parcel by mixing processes.

REFERENCES

- Anderson, J.G., W.H. Brune, S.A. Lloyd, D.W. Tooney, S.P. Sander, W.L. Starr, M. Loewenstein, and J.R. Podolske, 1989: Kinetics of O₃ destruction by ClO and BrO within the Antarctic vortex: An analysis based on in situ ER-2 data. *J. Geophys. Res.*, 94, 11480-11520.
- Brune, W.H., D.W. Tooney, J.G. Anderson, and K.R. Chan, 1990: In situ observations of ClO in the Arctic stratosphere: ER-2 Aircraft Results from 59°N to 80°N. *Geophys. Res. Lett.*, 17, 505-508.
- de Zafra, R.L., M. Jaramillo, A. Parrish, P. Solomon, B. Connor, and J. Barrett, 1987: High concentrations of chlorine monoxide at low altitudes in the Antarctic spring stratosphere: diurnal variation, *Nature*, 328, 408-411.
- Douglas, A.R., C.H. Jackman, and R.S. Stolarski, 1989: Comparison of model results transporting the odd nitrogen family with results transporting separate odd nitrogen species. *J. Geophys. Res.*, 94, 9862-9872.
- Fahey, D.W., S.R. Kawa, and K.R. Chan, 1989: Nitric oxide measurements in the Arctic winter stratosphere. *Geophys. Res. Lett.*, 17, 489-490.
- Jones, R.L., D.S. McKenna, L.R. Poole, and S. Solomon, 1989: Simulating the evolution of the chemical composition of the 1988/89 winter vortex. *Geophys. Res. Lett.*, 17, 549-552.
- Waters, J.W., L. Froidevaux, W.G. Read, G.L. Manney, L.S. Elson, D.A. Flower, R.F. Jarnot, and R.S. Harwood, 1993: Stratospheric ClO and ozone from the Microwave Limb Sounder on the Upper Atmosphere Research Satellite. *Nature*, 362, 597-602.